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# Possible Orientationally Ordered States of Bucky-Cubane

## Abstract

For temperatures above  $T^* = 130\text{K}$   $\text{C}_{60} \cdot \text{C}_8\text{H}_8$  forms a cubic crystal consisting of two interpenetrating fcc sublattices, one of freely rotating Buckys  $\text{C}_{60}$  and the other of orientationally ordered cubane  $\text{C}_8\text{H}_8$ . The crystal structure below a discontinuous transition is found to be orthorhombic, but the nature of the ordering of the Buckys has not yet been determined. Here possible orderings of the Buckys consistent with the size and symmetry of the orthorhombic unit cell are analyzed. Most likely inversion symmetry is preserved at the transition, in which case the small number of possible orderings are described. If inversion symmetry is removed, the point group can be  $\text{C}_{2v}$  which supports ferroelectricity or  $\text{D}_2$  which can be confirmed by proton NMR measurements.

## Disciplines

Physics

## Comments

This article can also be found on [arXiv:0902.2388](https://arxiv.org/abs/0902.2388)

# Possible Orientationally Ordered States of Bucky-Cubane

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(Dated: February 13, 2009)

For temperatures above  $T^* = 130\text{K}$   $\text{C}_{60}\cdot\text{C}_8\text{H}_8$  forms a cubic crystal consisting of two interpenetrating fcc sublattices, one of freely rotating Buckys  $\text{C}_{60}$  and the other of orientationally ordered cubane  $\text{C}_8\text{H}_8$ . The crystal structure below a discontinuous transition is found to be orthorhombic, but the nature of the ordering of the Buckys has not yet been determined. Here possible orderings of the Buckys consistent with the size and symmetry of the orthorhombic unit cell are analyzed. Most likely inversion symmetry is preserved at the transition, in which case the small number of possible orderings are described. If inversion symmetry is removed, the point group can be  $\text{C}_{2v}$  which supports ferroelectricity or  $\text{D}_2$  which can be confirmed by proton NMR measurements.

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## INTRODUCTION

Orientational ordering of molecules has been studied for many years.[1, 2] For the present work the most relevant studies concern the orientational ordering of the fullerenes  $\text{C}_{60}$ [3] into a  $\text{Pa}\bar{3}$  space group,[4, 5, 6] and the analogous ordering in solid  $\text{C}_{70}$ . [7, 8] More recently cubane ( $\text{C}_8\text{H}_8$ ) has been crystallized and its properties studied.[9, 10] Now[11, 12, 13] the structure I will call Bucky-cubane has been studied. This system forms a cubic crystal consisting of two interpenetrating fcc lattice, one consisting entirely of Bucky ( $\text{C}_{60}$ ) molecules and the other entirely of cubane molecules. For temperature in the range  $130 < T < 470\text{K}$  the cubane molecules are ordered with their four-fold axes parallel to the cubic axes of the crystal, whereas the Bucky molecules are orientationally disordered.[11, 12, 13] Below  $T^* = 130\text{K}$  the Buckys apparently orientationally order in an as yet undetermined pattern, but the unit cell (see Fig. 1a) is orthorhombic (o-) with **a** and **b** lattice constants which are nearly equal to  $\mathbf{a}_c/\sqrt{2}$  and **c** nearly equal to  $2\mathbf{a}_c$ , where  $\mathbf{a}_c$  is the cubic lattice constant just above  $T^*$ . [13] As noted in Ref. 13 this data makes it clear that the o-unit cell contains four molecules of each species. As in the case of pure  $\text{C}_{60}$ , [6] the possible ordered structures which are consistent with this information can be severely restricted.

In this paper I analyze such possible orientationally ordered structures under three fundamental assumptions, namely 1) the indexing to an o- unit cell having the volume appropriate to four Buckys per unit cell is correct, 2) the cubane molecules retain the static orientation they had for  $T > T^*$  and 3) the locations of the centers of all the molecules are only perturbatively deformed from their positions for  $T > T^*$ . There are three o- point groups,  $\text{D}_2$  (222),  $\text{C}_{2v}$  (mm2), and  $\text{D}_{2h}$  (mmm). If the orientational ordering transition were continuous, one could assert that only a single symmetry is broken at the transition, since breaking more than one symmetry would require the accidental degeneracy implied by a multicrit-

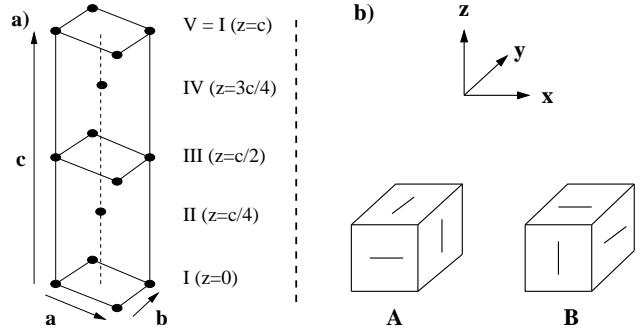


FIG. 1: a) The o- unit cell, showing only the Buckys, which form an fcc lattice when the Buckys rotate freely in which case  $a = b = \sqrt{2}c/4$  with  $a_c = \sqrt{2}a$  and the cubanes also form an fcc lattice. The Buckys form layers perpendicular to the  $c$ -axis labeled I-V, as shown. b) The two standard orientations of the icosahedron with 12 vertices within a circumscribed cube relative to the o- axes  $x$ ,  $y$ , and  $z$ . [14] Only edges of the icosahedron within the faces of the cube are shown. The other edges of the icosahedron are formed by joining adjacent ends of the edges which lie in the cube faces.  $\text{C}_{60}$  is an inversion symmetric truncated icosahedron, formed by cutting off each of the twelve vertices leaving a pentagonal face to yield a structure with 60 vertices.

ical point. This reasoning does not apply, of course, to a discontinuous transition as one has here. However, I regard it is less likely to break more than one symmetry at a time and therefore I deem it less likely, but still possible, that the point group of the ordered phase is  $\text{D}_2$  or  $\text{C}_{2v}$ , both of which lack inversion symmetry. In principle, the point group can be determined by macroscopic measurements. For instance, only the point group  $\text{C}_{2v}$  permits a spontaneous polarization. In the unlikely event this is the point group of Bucky-cubane for  $T < T^*$ , one would have the fascinating appearance of ferroelectricity driven by molecular ordering. Otherwise, in principle, one can distinguish between the other two point group by NMR experiments, since in  $\text{D}_2$  the unit cell contains eight inequivalent proton sites, whereas in  $\text{D}_{2h}$  there are only

four inequivalent proton sites. (The protons are at non-special positions, so the number of inequivalent protons is equal to the total number of protons in the unit cell divided by the number of space group elements.)

In the remainder of this paper, I will concentrate on the scenario I deem the most likely, namely that the point group for  $T < T^*$  is  $D_{2h}$ . In that case, I find that there are four possible space groups. In one of these the allowed orientations of the Buckys are quantized, whereas in the other three, the orientations of the Buckys are characterized by a rotation angle  $\phi$  relative to a “standard” orientation (see Fig. 1b) of the  $C_{60}$  molecule. Identifying these structures drastically reduces the number of fitting parameters and should facilitate a definitive structural analysis from scattering data.[15]

This paper is organized as follows. First I make some remarks on the nature of orientational ordering. Then I analyze, for the most likely point group  $D_{2h}$ , the possible structures within the four allowed space groups.

## GENERAL REMARKS

As noted in Ref. [13] the appearance of a structure in which the cubanes are orientationally ordered but the Buckys are orientationally disordered is explained by the orientational potential on the Buckys being dominated by the cubane-Bucky interaction. However, they also say that “The effect of interfullerene interactions is negligible, as such interactions would prefer the formation of the simple cubic  $Pa\bar{3}$  space group...” I suggest that the Bucky ordering does result from Bucky-Bucky interactions in combination with the larger single molecule terms, as is reflected in the structure of the generalized orientational Landau free energy

$$F = \sum_{M,N,\mathbf{q}} [\chi(M, N, \mathbf{q})]^{-1} Q_6^M(\mathbf{q}) Q_6^N(-\mathbf{q}) + \mathcal{O}(Q^3) \quad (1)$$

where  $Q_6^M(\mathbf{q})$  is the spatial Fourier transform of the order parameter  $Q_6^M(\mathbf{q})$ , a sixth rank tensor which characterizes, at lowest tensor order, the orientational fluctuations of the Buckys[6] and  $[\chi(M, N, \mathbf{q})]^{-1}$  is the inverse orientational susceptibility. Here I do not include terms involving products of three or more order parameters or higher order tensor order parameters. The first point is that if one has a sharp orientational ordering transition, this can not be caused solely by a single molecule potential on the Buckys due to their interactions with the cubanes. Although the orientational transition is not continuous, I nevertheless expect that the instability toward ordering is signalled by the minimum in  $[\chi]^{-1}$ . While it is true that this minimum leads to  $Pa\bar{3}$  ordering in pure  $C_{60}$ , here the single molecule terms can shift the minimum to one corresponding to the actual ordering in Bucky-cubane. The Bucky-Bucky interactions must determine

the long-range order, as otherwise structures in which an entire plane of Buckys are in the A standard orientation would not be favored over some a distribution of A and B orientations. Here I will not attempt any calculations of the orientational susceptibility,  $\chi(M, N, \mathbf{q})$ .

The formal theory outlined above can, in principle, lead to a prediction of the orientationally ordered structure. In addition, one can also consider coupling of the orientational order parameters to various elastic degrees of freedom, such as strains and zero wave vector optical phonons. Consider, for instance, the orientational strain interaction,  $V_{OS}$  of the form

$$V_{OS} \sim \text{const} |Q|^2 \epsilon, \quad (2)$$

where  $\epsilon$  is a component of the strain tensor. As soon as ordering in  $Q$  develops, this term induces a strain  $\epsilon$  of order  $|Q|^2$ . Rather than develop the details of such a theory, it is far simpler simply to look at the symmetry of the orientational ordering to infer the components of strain it must induce. This approach is adopted below. Similarly, I will deduce the displacements within the unit cell which are induced by orientational ordering.

## ALLOWED $D_{2h}$ STRUCTURES

The approach I adopt is as follows. I initially assume that the positions of the centers of all molecules are the same in the o- phase as in the cubic phase, the cubanes assume the same orientations as in the cubic phase, and that the Buckys assume fixed orientations. Only certain o- space groups permit this. For each allowable space group I determine the possible orientations of the Buckys consistent with the space group symmetry. Then since the unit cell no longer has cubic symmetry, it must distort into the actual o- structure. Also, the molecules would suffer very small (possibly undetectable) distortions because their high molecular symmetry is broken by the much lower symmetry of the sites they occupy. Finally, the positions of the centers of the molecules within the unit cell may be less restricted in the o- structure than in the cubic structure. Of course, I will not estimate these distortions, but, in the case of the positions of the molecular centers, will only note their symmetry.

We wish to determine which space groups can accommodate sites at  $\mathbf{r}_1 = (0, 0, 0)$ ,  $\mathbf{r}_2 = (1/2, 1/2, 1/4)$ ,  $\mathbf{r}_3 = (0, 0, 1/2)$ , and  $\mathbf{r}_4 = (1/2, 1/2, 3/4)$  in terms of fraction of the lengths of the o- unit cell, shown in Fig. 1a. These coordinates must be interpreted as being coordinates relative to an arbitrary origin which need not be the same as that used in the listing in Ref. 16. I found it convenient to make this identification in two stages. In the first stage I looked for Wyckoff orbits (generated by the space groups elements) of four sites in the unit cell which reproduce the above  $\mathbf{r}_n$ . Many such orbits can immediately be rejected. For instance, orbits confined to a

TABLE I: Allowed space groups (numbered as in Ref. 16) for the inversion symmetric o- point group  $mmm$ . The  $r_\alpha$  are the displacement (glide) vectors for the mirror  $m_\alpha$ .

S. G. #	$r_x$	$r_y$	$r_z$
Pmmm (47)	(0,0,0)	(0,0,0)	(0,0,0)
Pccm (49)	(0,0,1/2)	(0,0,1/2)	(0,0,0)
Pcmm (51)	(0,0,1/2)	(0,0,0)	(0,0,1/2)
Pccn (56)	(1/2,0,1/2)	(0,1/2,1/2)	(1/2,1/2,0)

single plane obviously are rejected. Also, one of the coordinates (not necessarily  $z$ ) should assume values close to  $z_0$ ,  $z_0 + 1/4$ ,  $z_0 + 1/2$  and  $z_0 + 3/4$  in the orbit. The only space group having a single orbit which can reproduce the  $r_n$  is Pccn (#56) which gives the orbit

$$\left(\frac{3}{4}, \frac{3}{4}, -z\right) \quad \left(\frac{1}{4}, \frac{1}{4}, z\right) \quad \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{2} - z\right) \quad \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{2} + z\right). \quad (3)$$

If one sets  $z = 1/8$  and adds  $(-3/4, -3/4, 1/8)$  to the above sites, then one gets the desired  $r_n$ .

We can also reproduce the desired  $r_n$  using orbits of one or two sites. For instance, in Pmmm (#47) we have the sites (each orbit is enclosed by a square bracket)

$$[(0, 0, 0)] \quad [(0, 0, \frac{1}{2})] \quad [(\frac{1}{2}, \frac{1}{2}, z)] \quad [(\frac{1}{2}, \frac{1}{2}, 1 - z)] \quad (4)$$

where  $z = 1/4$  gives the desired set of sites. Also, in Pccm (#49) we have the sites

$$[(0, 0, 0)] \quad [(0, 0, 1/2)] \quad [(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})] \quad [(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})] \quad (5)$$

and in Pcmm (equivalent to Pmma, #51) we have the sites

$$[(0, 0, 0)] \quad [(0, 0, 1/2)] \quad [(x, \frac{1}{2}, \frac{1}{4})] \quad [(-x, \frac{1}{2}, \frac{3}{4})], \quad (6)$$

where  $x = 1/2$  gives the desired set of sites.

It remains to determine the allowed orientations of the Buckys on the sites of each of the four allowed space groups. To do that I show, in Fig. 1b, the “standard” orientations of a Bucky to be those for which each o- direction coincides with a two-fold axis of the Bucky. (The Bucky has other two-fold axes, but those are in nonspecial directions relative to the o- axes.) Also, in Table I are listed the displacement (glide) vectors associated with each mirror  $m_\alpha$  (which reverses the sign of the  $\alpha$  coordinate) for the space groups in question. Note: the glide vectors depend on the choice of origin and our choice in Eqs. (3-6) is the same as that of Ref. 16.

#### Space Group #47, Pmmm

First consider space group #47. The Bucky sites in layers I and III have mirror planes perpendicular to the o-

axes. So the edges of the Bucky cubes of Fig. 1b coincide with the o- axes. Thus all Buckys in layer I must either be standard orientation A or orientation B and similarly for sites in layer III. The Bucky sites in layers II and IV with  $z = 1/4 + \delta$  for small  $\delta$  have two mirrors and are interrelated by the remaining mirror. The presence of these mirrors force all these molecules to be in the same standard orientation. So the five layers of Buckys perpendicular to the  $c$  axis (labeled I-V in Fig. 1a) can either be

$$S_1 = A, A, A, A, A \quad \text{or} \quad S_2 = A, A, B, A, A \\ \text{or} \quad S_3 = A, B, A, B, A. \quad (7)$$

(The roles of A and B can be interchanged within the same structure.) In structure  $S_1$ ,  $\delta = 0$  is not allowed, lest one have a unit cell of side  $c/2$ . This same requirement holds for the structure  $S_3$ . In all cases here and below, the  $a$  and  $b$  directions are inequivalent because of the Bucky orientations as is apparent from Fig. 2.

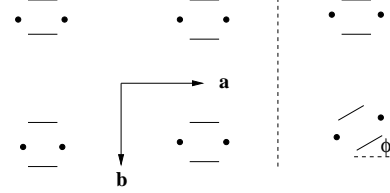


FIG. 2: Left: A plane perpendicular to the  $c$ -axis with all Buckys in the same standard orientation. Only the edges on the faces of the circumscribed cube of Fig. 1b not perpendicular to the  $c$ -axis are shown. The dots represent edges parallel to the  $c$ -axis. Clearly, the  $a$  and  $b$  directions are no longer equivalent in the presence of the orientationally ordered Buckys. Right: the lower Bucky is rotated through an angle  $\phi$  relative to the upper Bucky which is in a standard orientation.

We make some further comments about the structure  $S_n$ . Structure  $S_1$  requires simultaneously breaking orientational symmetry and enlarging the primitive unit cell. If the orientational transition were continuous, this would require a multicritical point, which one would reject because one never allows an accidental degeneracy of instability. But all bets are off for a first order transition. The same comments apply to structure  $S_3$ . Structure  $S_2$  will automatically have a distortion ( $\delta \neq 0$ ) because layer II is not a mirror plane. So structure  $S_2$  is the only one which does not require the simultaneous breaking of two symmetries and is therefore preferred on that ground. However, the o- structure has very different values for the lattice constants:  $a = 9.99\text{\AA}$  and  $b = 10.82\text{\AA}$ . [13] Structure  $S_2$  has three A layers which cause one sign of the strain making  $a - b$  nonzero and a single B layer which favors the other sign of  $a - b$ . In contrast, structure  $S_1$  has four A layers and therefore would seem more likely in view of the large value of  $a - b$ . Similarly structure  $S_3$  is

very bad from that point of view. However, in principle all three structures are consistent with existing information. Also note that the Bucky and cubane molecules are distorted when embedded in the crystal so as to be consistent with the lower symmetry of the sites they occupy.

### Space Group #49, Pccm

Note that all the mirror operations take layer II into layer IV, so, by considering the product of two mirrors we conclude that the sites in layers II and IV have three two-fold axes parallel to the  $o$ -axes. So these Buckys must all be in the same standard orientation. Only the mirror  $m_z$  takes the Bucky in layer I into itself. So, the Bucky in layer I is obtained from the standard orientation  $A$  by a rotation through an angle  $\phi_z$  about the  $c$  axis. This orientation is  $A(\phi_z)$ , where  $A(\phi_\alpha)$  denotes an orientation obtained from standard orientation  $A$  by a rotation through an angle  $\phi_\alpha$  about the  $\alpha$ -axis. The mirrors about  $x$  and  $y$  which take layer I into layer III imply that layer III has orientation  $A(-\phi_z)$ . So one has

$$S_4 = A(\phi_z), A, A(-\phi_z), A, A(\phi_z) \\ \text{or } S'_4 = A(\phi_z), B, A(-\phi_z), B, A(\phi_z). \quad (8)$$

Structures of type  $S_4$  and  $S'_4$  are equivalent under a four-fold rotation about the  $c$  axis and a relabeling of axes. Here  $\phi_z$  can not assume the special values  $\phi_z = 0$  or  $\pi/2$ , lest the unit cell contain only two Buckys.

### Space Group #51, Pmmm

The sites in layers I and III have the mirror  $m_y$  and are related by the mirrors  $m_x$  and  $m_z$ , so their orientations are  $A(\phi_y)$  and  $A(-\phi_y)$ , respectively. The site symmetry of the sites in layers II and IV comprises mirror planes  $m_y$  and  $m_z$  and are interrelated by  $m_x$ . Therefore these Buckys are all in the same standard orientation. However, the Buckys in layer II are at  $x = 1/2 + \epsilon$  and those in layer IV are at  $x = 1/2 - \epsilon$ , where  $\epsilon$  is small. So the orientations within the layers are

$$S_5 = A(\phi_y), A, A(-\phi_y), A, A(\phi_y) \\ \text{or } S'_5 = A(\phi_y), B, A(-\phi_y), B, A(\phi_y). \quad (9)$$

Structures of type  $S_5$  and  $S'_5$  are equivalent under a four-fold rotation about the  $c$  axis and a relabeling of axes. Here  $\phi_y = \epsilon = 0$  is not allowed lest the unit cell contain only two Buckys.

### Space Group #56, Pccn

We consider the sites of Eq. (3) with  $z = 1/8 + \eta$  for small  $\eta$ . This space group has a two-fold rotation  $m_x m_y$

about  $(1/4, 1/4, 0)$ , so the orientation of layer I is  $A(\phi_z)$ . The mirror  $m_z$  takes layer I into layer II and  $m_x$  (or  $m_y$ ) takes layer I into layer III and layer II into layer IV. These operations fix the orientation of the other layers in order of increasing  $z$  to be

$$A(\phi_z) \quad A(\phi_z) \quad A(-\phi_z) \quad A(-\phi_z) \quad A(\phi_z). \quad (10)$$

Note that  $\eta \neq 0$  because no symmetry forces  $\eta$  to vanish.

## SUMMARY

To summarize: point groups  $D_2$  and  $C_{2v}$  break inversion symmetry and therefore seem unlikely (but still possible) candidate structures for the phase in which the Buckys are orientationally ordered. If the phase is ferroelectric it is  $C_{2v}$ . If is not ferroelectric but NMR shows 8 inequivalent protons in the unit cell, then the phase is  $D_2$ . Otherwise, the orientations of the Buckys in space groups Pmmm, Pccm, Pmmm, and Pccn are given in Eqs. (7), (8), (9), and (10), respectively and the displacements of the layers are discussed in connection with these equations.

I thank J. E. Fischer for alerting me to this system and N. M. Nemes for helpful correspondence.

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